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1354471

PATENT SPECIFICATION

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(19)

(54) TETRAFLUOROETHYLENE POLYMERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to tetrafluoroethylene polymers and in particular to the modification of certain types of tetrafluoroethylene homopolymers or copolymers of tetrafluoroethylene with up to 10% by weight of a comonomer such as ethylene or hexafluoropropylene. For convenience such tetrafluoroethylene polymers and copolymers will be referred to hereinafter as PTFE.

PTFE is well known for its low friction properties and an increasing use of PTFE is as a dry lubricant powder for example in textile machinery. Such powders are also of use as lubricating or nucleating fillers for thermoplastics such as polyamides and polypropylene.

Heretofore suitable lubricant powders have been made by thermal degradation of PTFE, for example by heating in air, or in the presence of a degradation accelerator, at a temperature of the order of 500—600°C. Such thermally degraded PTFE powders may be comminuted, for example by milling, to a relatively small particle size but for some applications it would be desirable to decrease the size still further. Thus thermally degraded powders may be milled to a number average particle size of not less than 5 μm as measured optically. (The other well established technique of measurement of particle size of PTFE powders, namely the air permeability method, gives falsely low values for such thermally degraded powders and so partcle sizes specified herein are median number average particle sizes obtained by optical methods).

We have found that dry lubricant powders of finer particle size may conveniently be made by comminuation of certain types of PTFE after they have been irradiated.

According to one aspect of the invention we provide a process of converting a tetrafluoroethylene polymer into a form that is capable of being comminuted to a median number average particle size of less than 5 μm as measured optically which comprises subjecting an unsintered coagulated dispersion grade of a tetrafluoroethylene polymer selected from homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with up to 10% by weight based on the weight of the copolymer, of an ethylenically unsaturated comonomer, in powder form to γ-radiation until it has received a dose of at least 2 M Rads. The dose may be from 2 to 20 M Rads and the process may be conducted with the polymer initially at ambient temperature and in such a way that thermal degradation of the polymer is minimised.

According to another aspect of the invention we provide a process for the manufacture of a finely divided tetrafluoroethylene polymer comprising subjecting an unsintered coagulated dispersion grade of a tetrafluoroethylene polymer as defined above to γ-radiation as above set out and then comminuting the irradiated powder.

By the term "coagulated dispersion grade of a tetrafluoroethylene polymer" we mean those grades of PTFE obtained by the coagulation of an aqueous dispersion of PTFE made by the polymerisation of tetrafluoroethylene, optionally together with one or more comonomers, dispersed in an aqueous medium with the aid of an emulsifying agent which is generally highly fluorinated. The production of such PTFE dispersions is described in, inter alia, British Patent Specification 689,400. Such coagulated dispersion polymers are well known in the art. Examples of commercially available coagulated dispersion polymers are 'Fluon' CD1, CD4 and CDO42 sold by Imperial Chemical Industries Limited and "Teflon" 6 and 6C sold by E. I. du Pont de Nemours and Company. 'Fluon' and "Teflon" are trademarks.

Such coagulated dispersion polymers have a primary particle diameter of the order of 0.1 μm but as commercially available are somewhat sticky powders in the form of agglomerates having a mean diameter of the order of several hundred microns. Said powders are sticky in the sense that the powder can be compressed into a putty- or snowball-like material that can be broken into fibrous lumps. Shearing coagulated dispersion polymers in an attempt to reduce the particle size, for example by milling the powder, results in sticky fibrous products.

We have found that by subjecting these coagulated dispersion grades of PTFE to γ-irradiation the polymer is converted to a dry non-sticky fine friable powder that can easily be broken down, for example by rubbing between the fingers to a number average particle size of less than 5 μm.

In contrast to coagulated dispersion polymers that have not been irradiated, shearing, for example milling, of the irradiated polymer gives a more rounded, as opposed to fibrous, particle.

In practising the invention, after irradiation, the polymer powder may be comminuted by any suitable method, particularly by milling the irradiated powder either dry or in dispersion in a liquid.

The coagulated dispersion polymer may be irradiated by methods well known in the art. Convenient methods include irradiation by a Co^{60} source or by immersing the polymer sealed in a suitable container, for example an aluminium canister, in a spent fuel element pond.

The polymer powder should preferably be given a radiation dose of from 2 to 20 M Rads, more preferably 4 to 10 M Rads. The use of a higher dose would render the process uneconomic.

The invention is illustrated by the following Examples.

EXAMPLE 1

A quantity of 'Fluon' CD1 coagulated dispersion PTFE powder initially at ambient temperature was subjected to a dose of 5 M Rads of γ-irradiation in such a way that thermal degradation of the polymer was minimised. The resultant product was a friable fairly free flowing powder with a median number average particle size of the order of 5—10 μm measured optically.

On fine disintegration in a light oil using bead milling or equivalent liquid dispersion techniques an extremely fine powder was obtained with a median number average particle size of the order of 1—3 μm measured optically.

A polymer obtained by a thermal degradation process treated similarly gave a product with a median number average particle size of the order of 5—10 μ measured optically.

EXAMPLE 2

By way of comparison a quantity of a milled granular PTFE powder sold under the name 'Fluon' G163 was subjected to a dose of 5 M Rads of γ-irradiation. The resultant product was a friable fairly free flowing powder with a median number average particle size of the order of 5—10 μm measured optically. Fine disintegration in a fluid energy mill gave a powder with a median number average particle size which was still of the order of 5—10 μm measured optically.

A polymer obtained by the irradiation of 'Fluon' CD1 coagulated dispersion polymer gives a finer powder of less than 5 μm median number average particle size when treated similarly.

WHAT WE CLAIM IS:—

1. A process of converting a tetrafluoroethylene polymer into a form that is capable of being comminuted to a median number average particle size of less than 5 μm as measured optically which comprises subjecting an unsintered coagulated dispersion grade of a tetrafluoroethylene polymer selected from homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with up to 10% by weight, based on the weight of the copolymer, of an ethylenically unsaturated comonomer, in powder form to γ-radiation until it has received a dose of at least 2 M Rads.

2. A process according to claim 1 wherein the dose is from 2 to 20 M Rads.

3. A process according to claim 1 in which the dose is from 2 to 20 M Rads and the process is conducted with the polymer initially at ambient temperature and in such a way that thermal degradation of the polymer is minimised.

4. A process according to claim 2 wherein the polymer treated is a tetrafluoroethylene homopolymer, the dose is 5 M Rad and the process is conducted with the polymer initially at ambient temperature and in such a way that thermal degradation of the polymer is minimised.

5. A process according to claim 1 substantially as herein described with reference to either of the Examples.

6. A tetrafluoroethylene polymer that is capable of being comminuted to a median number average particle size of less than 5 μm as measured optically prepared by a process according to any one of the preceding claims.

7. An irradiated unsintered coagulated dispersion grade of a tetrafluoroethylene polymer selected from homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with up to 10% by weight, based on the weight of the copolymer, of an ethylenically unsaturated comonomer, the irradiated polymer being capable of being comminuted

to a median number average particle size of less than 5 μm as measured optically.

8. A polymer according to claim 7 substantially as herein described with reference to either of the Examples.

9. A process for the manufacture of a finely divided tetrafluoroethylene polymer comprising subjecting a polymer according to any one of claims 6 to 8 to a milling step in which it is milled either dry or in dispersion in a liquid.

10. A process for the manufacture of a finely divided tetrafluoroethylene polymer comprising subjecting an unsintered coagulated dispersion grade of a tetrafluoroethylene polymer selected from homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with up to 10% by weight, based on the weight of the copolymer, of an ethylenically unsaturated comonomer, in powder form to γ-radiation until it has received a dose of at least 2 M Rads and then comminuting the irradiated powder.

11. A process according to claim 10 wherein the dose is from 2 to 20 M Rads.

12. A process according to claim 10 wherein the dose is from 4 to 10 M Rads.

13. A process according to claim 10 wherein the polymer treated is a tetrafluoroethylene homopolymer and the dose is 5 M Rad.

14. A process as claimed in any one of claims 10 to 13 wherein the irradiated powder is comminuted by milling it dry or in dispersion in a liquid.

15. A process according to claim 10 substantially as hereinbefore described with reference to either of the Examples.

16. A finely divided tetrafluoroethylene polymer made by a process according to any one of claims 10 to 15.

17. An irradiated unsintered coagulated dispersion grade of a tetrafluoroethylene polymer in the form of finely divided particles of which the median number average particle size is less than 5 μm as measured optically wherein the tetrafluoroethylene polymer is selected from homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with up to 10% by weight, based on the weight of the copolymer, of an ethylenically unsaturated comonomer.

18. A tetrafluoroethylene polymer according to claim 17 substantially as hereinbefore described with reference to either of the Examples.

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